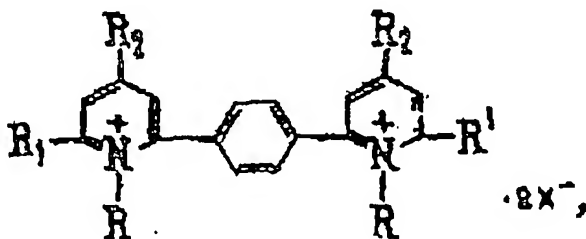Russian/Translation

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Title:

**DERIVATIVES OF 1,4-PHENYLENE DI-2',2"-PYRIDYLIUM
AS ELECTROCHROMIC SUBSTANCES AND ELECTROCHROMIC
COMPOSITION ON THEIR BASIS**

Summary:

1. Derivatives of 1,4-phenylene di-2'2"-pyridylium of the general formula

where a) $R=C_3$, $R_1=R_2=C_6H_5$,
$X=ClO_4$,
b) $R=CH_3$, $R_1=tert-C_4H_9$,
$R_2=C_6H_5$, $X=ClO_4$;
c) $R=CH_3$, $R_1=CH_3C_6H_4$, $R_2=C_6H_5$, $X=BF_4$,

as electrochromic substances.

2. Electrochromic composition containing a dipyridylium deriva-
tive, tert-butylferrocene, polymethyl methacrylate and γ-butyro-
lactone, characterized by the fact that for the purpose of
increasing the uniformity of the electromodulated absorption in the
visible range of the optic spectrum and expanding it in the near IR
range it contains as the dipyridylium derivative a derivative of
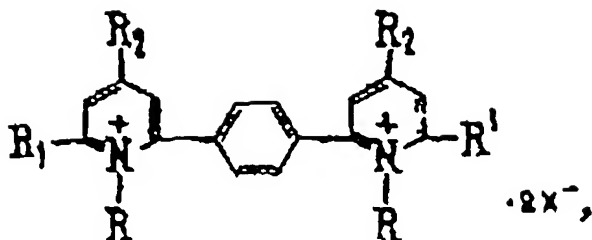1,4-phenylene di-2',2"-pyridylium of the general formula

where a) $R=C_3$, $R_1=R_2=C_6H_5$,
       $X=ClO_4$,
    b) $R=CH_3$, $R_1=tert-C_4H_9$,
       $R_2=C6_4H_5$, $X=ClO_4$;
    c) $R=CH_3$, $R_1=CH_3C_6H_4$,
       $R_2=C_6H_5$, $X=BF_4$,

with the following ratio of ingredients, wt.%: 1,4-phenylene di-2'-2"-pyridylium derivative: 0.8-3.0, tert.butyl ferrocene: 3.0-6.0, polymethyl methacrylate: 0.5-2.0, γ-butyrolactone: remainder

Description

The invention concerns new organic compounds, specifically derivatives of 1,4-phenylene di-2'-2"-pyridylium of the general formula
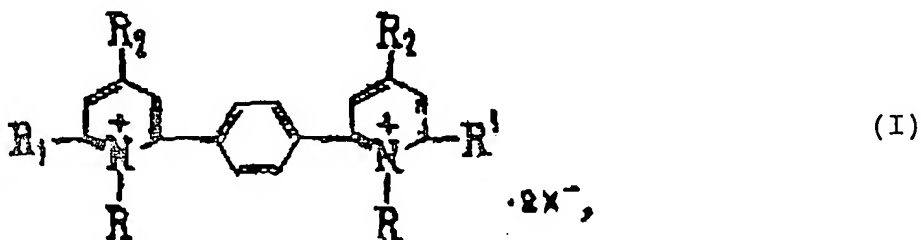

(I)

where a) $R=C_3$, $R_1=R_2=C_6H_5$, $X=ClO_4$,
b) $R=CH_3$, $R_1=tert-C_4H_9$,
$R_2=C_6H_5$, $X=ClO_4$;
c) $R=CH_3$, $R_1=CH_3C_6H_4$, $R_2=C_6H_5$, $X=BF_4$,

as electrochromic substances and an electrochromic composition on their basis which are used predominantly for the creation of instruments with variable light transmission which varies upon application of an electrical field, e.g., light filters of variable optic density for sunlight or laser radiation, stabilizers of various types of radiations, alphanumeric indicators on instruments etc.

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Electrochromic compositions which include as the electrochromic substance a quaternary salt of dipyridylium are well known.

The known compounds form highly reversible electrochromic redox systems, but the electrochromic compositions on their basis assure modulation of light only on individual segments of the visible range of the optic spectrum.

Of the known organic electrochromic compositions the closest is the composition which includes a quaternary salt of dipyridylium, tert.-butylferrocene, γ-butyrolactone (solvent) and polymethyl methacrylate (a substance which increases the viscosity).

However, the absorption spectrum of the electromodulated form of this composition consists predominantly of two absorption bands of varying intensity, one at the boundary of the near UV and visible range and the second in the visible range or at its boundary with the IR range and not overlapping with the entire visible range of wavelengths.

Therefore the previously known quaterinary salt of dipyridylium and compositions based on them do not assure uniformity of electromodulated absorption over the entire visible region of the spectrum (according to the type of a neutral light filter).

The purpose of the invention was to devise new compounds having electrochromic properties and an electrochromic composition on their basis with elevated uniformity of the electromodulated absorption over the entire visible range of the spectrum and expansion of this absorption in the near IR range.

This objective is achieved by the new derivatives of 1,4-phenylene di-2'-2"-pyridylium of formula I also by the fact that

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the electrochromic composition containing the dipyridylium derivative, tert.-butylferrocene, polymethyl methacrylate and γ-butyrolactone, contains as the dipyridylium derivative the derivative of 1,4-phenylene di-2'-2"-pyridylium of general formula I in the following ratio of ingredients, wt.%: derivative of 1,4-phenylene di-2'-2"-pyridylium 0.8-3.0, tert.butyl ferrocene: 3.0-6.0, polymethylmethacrylate: 0.5-2.0, γ-butyrolactone: remainder.

The derivatives of 1,4-phenylene di-2'-2"-pyridylium are obtained by reacting diethinyl benzene with the corresponding ketone in glacial acetic acid in the presence of hydrochloric acid or boron trifluoride etherate at a temperature of 117°C for a period of 10 minutes. The dipyridylium salt obtained is treated with an aqueous solution of methylamine while boiling for 1 hour.

1,4-phenylene di-2,2"-(1'-methyl-4',6'-diphenyl) pyridylium diperchlorate.

A mixture of 1.26 g (0.01 m) of diethinyl benzene (4.2 g of benzal acetophenone (0.02 m) and 2 ml of 70% $HClO_4$ (0.02 m) in 5 ml of glacial acetic acid is heated at 117°C for 10 min.

The mixture is cooled, diluted with ether, and 3.8 g of the dipyridylium salt are filtered off. The solution of dipyridylium salt in 50 ml of glacial acetic acid with 1.5 ml of a 25% aqueous solution of methylamine is boiled for 1 hour. It is cooled, diluted with ether and 2.58 g (65.78%) of product with a melting point of 284°C (isopropyl alcohol plus $HClO_4$) are filtered off. Calculated, %: C 65.9, H 4.44, Cl 9.18, N 3.66. $C_{42}H_{34}O_8Cl_2N_2$. Found: %, C 65.9, H 4.55, Cl 8.62, N. 3.49. IR spectroscopic data: 1100, 1620.

1,4-phenylene di-2'-2"-(1'-methyl-4'-phenyl-6'-tert.-butyl) pyridylium diperchlorate.

This is obtained in the same manner from diethinyl benzene and benzalpinacoline, melting point 256°C (isopropyl alcohol plus $HClO_4$). Yield: 73.22 %, Calculated, %: C 62.89, H 5.75, Cl 9.79, N 3.86. $C_{58}H_{42}O_8Cl_2N_2$. Found %:, C 63.01, H 5.89, Cl 9.63, N. 3.64. IR spectroscopic data: 1100, 1620.

1,4-phenylene di-2'-2"-(1'-methyl-4'-phenyl-6'-(4''''-methyl-phenyl)pyridylium ditetrafluoroborate.

Obtained in the same manner from diethinyl benzene, (4-methylbenzal acetophenone and boron trifluoride etherate. Melting point 25°C. Yield: 71.1% (isopropyl alcohol plus $HClO_4$). Calculated, %: C 68.75, H 4.94, F 19.79, N 3.64. $C_{46}H_{38}F_2B_2N_2$. Found %:, C 68.66, H 4.87, F 19.47, N. 3.55. IR spectroscopic data: 1080, 1615.

The technique for determining the uniformity of the electro-modulated absorption of the electrochromic compositions in the visible spectral range and the expansion of this absorption into the near IR range consists of the following. The electrochromic compositions are tested in a device consisting of two glass plates with films of In_2O_3 applied to the inner surface with alloying additives. The glass plates or disks are placed one on the other with a shifting in one of the directions which assures the possibility of attaching the contact to the conducting coatings. Between the glasses one places a Teflon frame. The space bounded by the Teflon frame and two glass plates is filled with electro-chromic composition. In the initial and electromodulated states

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one records the absorption spectra of the instrument in the wavelength interval of 350-750 nm. From the absorption spectra one determines the increase in optic density at λ=400, 500, 600 and 700 nm and then one calculates the arbitrary value of "a" --the ratio of the increase in the value of optic density of the electromodulated state at the selected wavelength, and λ=500 nm. In the case of ideal uniformity of the electromodulated absorption the values of "a" = 1 for all wavelengths. The experimental values of "a" of the electrochromic compositions are given in Table 1.

The expansion of the electromodulated absorption in the near IR range in the interval of 750-1200 nm is determined by comparing the spectra of the electromodulated absorption of the prototype and the claimed composition at voltages exceeding the threshold by 0.25 v. The threshold voltage in the case of the prototype is 0.6 v, but that of the composition according to the invention 1.15 v.

Example (prototype)

a) In a 0.5% solution of polymethylmethacrylate and γ-butyerolactone one dissolves 1,1-dimethyl-4,4,-dipyridylium diperchlorate (2% concentration) and a mixture of mono- di- and tri-) tert-butylferrocenes (6% concentration) and with the solution obtained one fills an electrochromic instrument with electrodes made of In_2O_3 spaced 0.02 cm apart. On the electrodes a voltage of 0.75 v is applied. From the absorption spectra in the initial and electromodulated states one determines "a" at λ=400, 600 and 700 nm which was found to be equal respectively to 23, 7 and 1.5 (see prototype, Table 1).

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b) An electrochromic device with electrodes of InN_2O_3 spaced at a distance of 0.02 cm was filled with the above noted composition (a). In the wavelength interval of 700-1200 nm the absorption spectra of the device was measured in the initial state and with application of a voltage of 0.85 v. The experimental data on the values of the optic densities for the initial and electromodulated states are presented in Table 2. The increase in the external voltage on the electrodes has practically no effect on the absorption in the wavelength range above 750 nm.

Example 1

1,4-phenylene di-2'-2"-(1'-methyl-4', 6'-diphenyl) pyridylium diperchlorate (0.8% concentration) and a mixture of (mono-, di-, tri-) tert-butyl ferrocenes (6% concentration) are dissolved in a 0.5% solution of polymethyl methacrylate in γ-butyrolactone and the solutions obtained are used to fill an electrochromic device as in the example (prototype). Upon application of a voltage of 1.3 v to the electrodes the uncolored composition assumes a neutral color. From the absorption spectra in the initial and electromodulated states one determines the value of "a" at $\lambda=400$, 600, 700 nm which was found to be equal respectively to 1.5, 1.47 and 1.07 (see sample 1, Table 1). When the voltage was removed the composition returned to the initial colorless state. The application of a controllable value of dc voltage and its removal entiails the controllable reproduction of the absorption spectra of the compositions in the initial and electromodulated state.

Example 2

1,4-phenylene di-2'-2"-(1'-methyl-4', 6'-phenyl) pyridylium (2% concentration) and a mixture of (mono-, di-, tri-) tert-butyl ferrocenes (6% concentration are dissolved in a 0.5% solution of polymethyl methacrylate in γ-butyrolactone and the solutions obtained are used to fill an electrochromic device as in example 1. A voltage of 1.4 V is applied to the electrode. The optic densities at λ=400, 500, 600 and 700 nm determined from the absorption spectra of the electromodulated state were repspectively 1.5, 1.5 and 1.25 (see sample 2, Table 1). Upon removal of the voltage the composition returns to the initial colorless state. The application of a controllable value of dc voltage and its removal is accompained by controllable reproduction of the absorption spectra of the composition in the initial and electro-modulated states.

Example 3

1,4-phenylene di-2'-2"-(1'-methyl-4',6'-phenyl) pyridylium perchlorate (3% concentration) and a mixture of (mono-, di-, tri-) tert-butyl ferrocenes (6% concentration are dissolved in a 0.5% solution of polymethyl methacrylate in γ-butyrolactone, and the solutions obtained are used to fill an electrochromic device as in example 1. A voltage of 1.3 V is applied to the electrode. The optic densities at λ=400, 600, and 700 nm determined from the absorption spectra of the initial and electromodulated states were repspectively 1.78, 1.68 and 1.25 (see sample 3, Table 1). Upon removal of the voltage the composition returns to the initial colorless state. The application of a controllable value of dc

voltage and its removal is accompained by controllable reproduction
of the absorption spectra of the composition in the initial and
electromodulated states.

Example 4

1,4-phenylene di-2'-2"-(1'-methyl-4'-phenyl-6'-tert.butyl)
pyridylium diperchlorate (2% concentration) and a mixture of
(mono-, di-, tri-) tert-butylferrocenes (5% concentration are
dissolved in a 1% solution of polymethyl methacrylate in γ-
butyrolactone and the solutions obtained are used to fill an
electrochromic device as in example 1. When a voltage of 1.4 V is
applied to the electrode the colorless composition assumes a
neutral color. The optic densities at λ=400, 600, and 700 nm
determined from the absorption spectra of the initial and electro-
modulated state were repspectively 1, 1 and 1.95 (see sample 4,
Table 1). Upon removal of the voltage the composition returns to
the initial colorless state. The application of a controllable
value of dc voltage and its removal is accompained by controllable
reproduction of the absorption spectra of the composition in the
initial and electromodulated states.

Example 5

1,4-phenylene di-2'-2"-(1'-methyl-4'-phenyl-6'(4"-methyl-
phenyl). pyridylium ditetrafluoroborate (1% concentration) and a
mixture of (mono-, di-, tri-) tert-butylferrocenes (3% concentra-
tion are dissolved in a 2% solution of polymethyl methacrylate in
γ-butyrolactone and the solution obtained is used to fill an
electrochromic device as in example 1. Upon application of a
voltage of 1.4 V to the electrode the composition assumes a nearly

neutral color. The optic densities at $\lambda=400$, 600, and 700 nm determined from the absorption spectra of the initial and electro-modulated state were repspectively 1, 1.05 and 1.7 (see sample 5, Table 1). Upon removal of the voltage the composition returns to the initial state. The application of a controllable value of dc voltage and its removal is accompained by controllable reproduction of the absorption spectra of the composition in the initial and electromodulated states.

Example 6

1,4-phenylene di-2'-2"-(1'-methyl-4'-phenyl-6'-tert.butyl) pyridylium diperchlorate and 1,4-phenylene di-2',2"(1'-ethyl-4'-6'-diphenyl) pyridinium diperchlorate (0.3 and 1.2% concentrations respectively) and a mixture of (mono-, di-, tri-) tert-butyl ferrocenes (3% concentration) are dissolved in a 2% solution of polymethyl methacrylate in γ-butyrolactone and the solution obtained is used to fill an electrochromic device as in example 1. A voltage of 1.5 V is applied to the electrode. The optic densities at $\lambda=400$, 600, and 700 nm determined from the absorption spectra of the initial and electromodulated state were repspec-tively 1.23, 1.35 and ~1.4 (see sample 6, Table 1). Upon removal of the voltage the composition returns to the initial state. The application of a controllable value of dc voltage and its removal is accompained by controllable reproduction of the absorption spectra of the composition in the initial and electromodulated states.

Example 7

1,4-phenylene-di-2'-2"-(1'-methyl-4'-phenyl-6'-tert.butyl)
pyridylium diperchlorate and 1,4-phenylene di-2',2"(1'-methyl-4'-
6'-diphenyl) pyridylium diperchloroate (both in a 1% concentration)
and a mixture of (mono-, di-, tri-) tert-butylferrocenes (3%
concentration) are dissolved in a 0.5% solution of polymethyl
methacrylate in γ-butyrolactone and the solutions obtained are used
to fill and electrochromic device with electrodes of In_2O_3 spaced
at 0.02 cm. In the wavelength interval of 700-1200 nm one measures
the absorption of the device in initial state and upon application
of 1.40 v. The experimental data of the optic densities for both
states which are given in Table 2 show that the wavelength boundary
of the electromodulated absorption is at λ=11.50 nm. A increase in
the voltage leads to an increase in the absorption in the near
infrared range, and switching off the voltage returns the composi-
tion to its initial state.

Example 8

An electrochromic composition as in Example 7 with an optic
density in the electromodulated state close to unity is irradiated
for 6 hours with light of the wavelength interval of 380-3000 nm at
an intensity of 200 mW/cm^2. After the irradiation is completed and
the voltage switched off the electrochromic composition passes into
the colorless state with the initial absorption spectrum.

As may be seen from a comparison of the known composition and
the composition according to the invention the introduction of the
synthesized compounds permits one to obtain an electrochromic
composition with elevated uniformity of the electromodulated
absorption throughout the entire visible range of the spectrum

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according to the type of a neutral light filter with a coefficient "a" no higher than 1.4. A comparison with the known electrochromic composition having a wavelength boundary of abosorption of λ=750 nm shows expansion of the electromodulated absoption in IR range of the composition according to the invention up to λ=1150 nm. The composition according to the invention manifests photostability under conditions of irradiation. The sum total of the properties listed above permit one to create a universal light filter of variable optic density and electrical controls.

Table 1

Sample No.	U, V	d, cm	"a"		
			400 nm	600 nm	700 nm
Prototype	0.75	0.02	23	7	1.5
1	1.3	0.02	1.5	1.47	1.07
2	1.4	0.02	1.5	1.5	1.25
3	1.3	0.02	1.78	1.68	1.25
4	1.4	0.02	1	1	1.95
5	1.4	0.02	1	1.05	1.7
6	1.5	0.02	1.23	1.35	1.4

where U is the value of the voltage applied to the electrochromic device expressed in volts, d is the thickness of the sample, cm, a is the ratio of the increase in the values of the optic density of the composition in the electro-modulated state at the selected wavelength (%, nm) and λ=500 nm.

Table 2.

Sample No.	d, cm	U, V	λ, nm											
			D											
			700	740	780	820	860	900	940	980	1050	1100	1150	1200
Prototype	0.02	0.00	0.09	0.09	0.09	0.11	0.13	0.14	0.16	0.18	0.74	0.29	0.36	0.45
	0.02	0.85	0.52	0.35	0.22	0.19	0.20	0.21	0.23	0.23	0.27	0.31	0.37	0.47
Claimed composition	0.02	4.0	0.13	0.12	0.12	0.12	0.14	0.16	0.18	0.20	0.26	0.31	0.39	0.57
	0.02	1.4	1.3	1.4	1.37	1.2	1.04	0.9	0.77	0.68	0.6	0.58	0.62	0.69

where D is the optic density, λ is the wavelength nm, U, V is the value of the applied voltage in the device expressed in voltes, d is the thickness of the sample, cm.

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